REMOVAL OF WATER FROM NATURAL GAS USING ZEOLITE 4A AND ZEOLITE 5A

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CERTIFICATION OF APPROVAL

Removal of Water from Natural Gas Using Zeolite 4A and Zeolite 5A

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NORWAHYU BINTI JUSOH

ABSTRACT

This report is discussed regarding the research on Removal of Water from Natural Gas using Zeolite 4A and Zeolite 5A. The natural gas that comes from the well usually is saturated with water. Tri-ethylene glycol (TEG) is being used for many decades in the industry as one of the absorbent in removing water from natural gas but there are some problems and difficulties when dealing with this type of absorbent. Therefore, this project is conducted to find the alternatives in removing water from natural gas and to evaluate whether zeolites can be practiced and applied for offshore practices. Zeolites have been proved that they able to remove carbon dioxide from natural gas. A lot of research done proves that zeolites have a big potential to remove water vapour from natural gas effectively. To know the properties of chosen zeolites, characterization by using Surface Area Analyzer, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Field-Emission Scanning Electron Microscope (FESEM) and Thermogravimetric Analyzer (TGA) has been executed. Surface Area Analyzer is used to determine pore size and pore volume. Zeolite 4A has higher surface area, pore diameter and micropore volume compared to Zeolite 5A. Both of zeolites exhibit monolayer and chemisorption type of adsorption. XRD shows that Zeolite 4A is more crystal than Zeolite 5A. Both of zeolites are cubic crystal system with identical lattice parameters. XRF is performed to know the elemental composition in zeolites and from the result, it is confirm that Zeolite 4A in a sodium form and Zeolite 5A in a calcium form. FESEM is executed to observe the morphology of the zeolite. From the image obtained, pore size and interconnecting pores of Zeolite 5A seems bigger than Zeolite 4A. TGA result shows both zeolites have higher degradation temperature than 900 °C. It was concluded that by using certain techniques, Zeolite 4A and Zeolite 5A can be identified for their pore area and pore volume, structure properties, elemental composition, morphology and thermal stability. Dynamic Performance Study has been conducted by varying pressure20 to 60 bar, with constant flowate of 5LPM and constant temperature of 50°C in order to study the performance of the zeolites in removing water from natural gas. The best zeolite was selected based on adsorbent capacity and percentage of removing water from natural gas. It was concluded that lower pressure give better result since it give higher adsorption capacity and total water of

removal from natural gas. Zeolite 5A is found give better performance in removing water from natural gas than Zeolite 4A due to its affinities towards water.

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Natural gas is one of a vital element of the world's supply of energy. It is clean, safe, and most useful of all energy sources (Natural Gas, 2009). Natural gas comes from three sources which are from oil wells, gas wells and condensate wells. The gas from oil wells is free gas or dissolved gas and is usually termed as associated gas. Meanwhile, the gas that comes from gas and condensate wells is called as non associated gas in which there is little or no crude oil (NaturalGas, 2004).

Commonly the natural gas from the wells is saturated with the water (NaturalGas, 2004). It is necessary to remove most of the associated water because the presence of water in natural gas can leads to the corrosion phenomena due to reaction with hydrogen sulphide or carbon dioxide in forming acid carbonate. The natural gas also has a tendency to form the hydrates which is in a solid form when temperatures drop. The formation of hydrates can caused plugging of valves, piping and etc (Kh. Mohamadbeigy et.al, 2007).

Condensation of water vapour in natural gas can caused the obstruction of the slug flow which is leads to the possible erosion and corrosion. Besides that, the water vapour gives the effects for the volume of natural gas and decreases the heat value of the gas. The water supposed to be removed from natural gas in order to meet dew point requirement of sales gas contract or pipeline specifications which is maximum water content usually 6 to 7 lb of water per mmscf (P.Ghandidasan et.al, 2000)].

This project is focused on the removal of water from natural gas using Zeolite 4A and Zeolite 5A. Zeolite is an adsorbent consists of tiny pores and uniform size that has a potential as an adsorbent for gases and liquids.

1.2 PROBLEM STATEMENT

Currently, Tri-ethylene glycol (TEG) is being used in the industry to remove water from natural gas. TEG is one of the liquid desiccants that have a great affinity for water. The hydroxyl and ether groups in glycols form some similar characteristics with water molecules (P.Ghandidasan et.al, 2000)].

Even though the TEG is good for removing water from natural gas, but there are some problems and difficulties when dealing with this type of desiccant (P.Ghandidasan et.al, 2000)]. The one of the major problem is difficult for installation since it requires higher and bigger equipment such as contactor tower. Contactor tower can be 12 metres high and it is used for the absorption process where the gas is contacted with glycol flowing downward across the trays or through the packed bed.

The other problems when operated TEG are glycol solutions can contaminated by suspended foreign matter such as dirt, scale and etc. Besides that, overheating of the solutions leads to the low and high boiling decompositions products. Glycol solution with high concentration has a tendency to become viscous at low temperature which leads to the pumping process difficulties and this solution has a potential to completely solidify when the (P.Ghandidasan et.al, 2000).

Therefore, this project is come out to judge the viability and suitability of compact new dehydration system using zeolite for removing water from natural gas purpose. As a solution to above problem, research need to find the alternatives in removing water from natural gas instead of TEG.

Zeolites have been proved that they able to remove carbon dioxide from natural gas. A lot of research done proves that zeolites have a big potential to remove water vapour from natural gas effectively. The characterization and dynamic performance study is executed to study the performance of zeolite in removing water from natural gas.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this project are:

1. To carry out characterization studies of chosen zeolites which are Zeolite 4A and Zeolite 5A.

2. To execute dynamic performance study in order to study the affect of pressure to the performance of the system in removing water from natural gas.

3. To assess the viability and suitability of compact new dehydration system using zeolite for removing water from natural gas purpose.

4. To chose the best zeolite (Zeolite 4A or Zeolite 5A) regarding the ability of removing water from natural gas. The performance of the system is evaluated based on adsorption capacity and percent of water removal by zeolites.

1.4 SCOPE OF STUDY

Through this project, Zeolite 4A and 5A performance as potential adsorbent will be determined from their capabilities of removing the water from natural gas. The research will study the characterization based on their physical and chemical properties of these adsorbents by performing several methods; Surface Area Analyzer, Thermogravimetric Analysis (TGA), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Field Emission Scanning Electron Microscopy (FESEM).

Besides that, the dynamic performance of the adsorbent will be analyzed by adjusting parameter; pressure. The performance of the system is evaluated based on adsorption capacity and percent of water removal by zeolites. The performance of Zeolite 4A and Zeolite 5A will be compare to define which one is the best adsorbent.

CHAPTER 2
LITERATURE REVIEW

2.1 NATURAL GAS

Natural gas is a colorless, shapeless and odorless in its pure form. It is a combustible mixture of hydrocarbon gases and gives great of energy sources when it burned. The table below shows the composition of typical natural gas: (NaturalGas, 2004)

Components	Chemical formula	Composition
Methane	CH_4	70-98%
Ethane	C_2H_6	1-10%
Propane	C_3H_8	Trace – 5%
Butane	C_4H_{10}	Trace – 2%
Pentane	C_5H_{12}	Trace – 1%
Hexanes	C_6H_{14}	Trace – 0.5%
Heptanes plus	C_7H_{16}	Trace – 0.5%
Nitrogen	N_2	Trace – 15%
Carbon dioxide	$C0_2$	Trace – 5%
Hydrogen sulfide	H_2S	Trace – 3%
Helium	He	Trace (5%) or none

Table 2.1: The components and compositions of natural gas

2.2 ABSORPTION AND ADSORPTION PROCESS

The operation of using liquid desiccant such as Tri-ethylene glycol (TEG) applied absorption process (P. Gandhidasan et.al, 2000) Absorption process is a separation of particles of gas or liquid which is called as solute or absorbate to the liquid surface which is called as solvent or absorbent. Throughout this process, molecules are taken up by the volume and not by the surface and it basically involves chemical reaction (Andrew Knight, 1996).

For this project, the selected adsorbent is applying adsorbent process. Adsorption process is a separation of components in fluid mixtures by the transfer of one or more components called adsorbates (water vapour from natural gas) to the internal surface of a porous solid identified as the adsorbent where they are held by intermolecular forces. This process is a surface phenomenon and does not involve any chemical reaction (Andrew Knight, 1996).

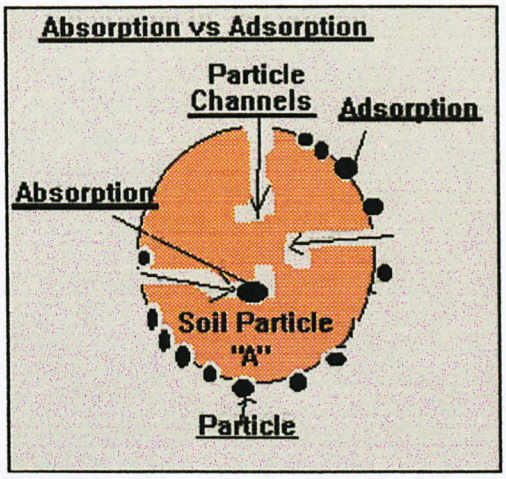

Figure 2.2: Difference between absorption and adsorption process.

2.3 SOLID DESICCANTS

Solid desiccants can be characterized as an internal porous structure that contains very large internal surface areas with very small radii of curvature. The good solid desiccants for removing water from natural gas must possess a high bulk of density for the components to be removed. They also should have a large surface area for high capacity and good mass transfer rate. (Pramatha Payra et.al, 2003)

Another criteria that should adsorbents have is possess high mechanical strength to resist crushing and dust formation. Since the unit cost is sensitive to the pressure drop, therefore, it is good for the adsorbents to have small resistance to gas flow through the desiccant bed in order to get low pressure drop. Besides that, they must be cheap, non-toxic, non-corrosive and chemically inert (P.Gandhidasan et.al, 2000).

The good adsorbents must be easily and economically regenerated and no appreciable change in volume during adsorption and desorption. The potential solid desiccants used for removing water from natural gas are alumina, silica gel and molecular sieves.

Figure 2.3: Activated alumina balls (left) and Silica gel white

2.4 TYPES OF SOLID DESICCANT

2.4.1 Activated Alumina

Activated Alumina is made of aluminium oxide (Alumina: Al_2O_3) by dehydroxylating aluminium hydroxide and consequently producing highly porous material. It can have a significant surface area over 280 m^2/g ("Hydrates-Inhibition-Dehydration,"2009). This type of desiccant has been used to adsorb the water since its surface forces prefer water and it also has been applied as a filter of fluoride, arsenic and selenium and drinking water.

Activated alumina has a lot of small pores since it has a very high surface area to weight ratio. It also can hold alcohols, glycols ad heavy hydrocarbon. Operating with activated alumina requires large towers for water load. Thus, it will increase capital cost and head load but this type of adsorbent has its advantages which is its physical strength is strongest and toughest compared to other adsorbents such as activated carbon, silica gel, activated alumina and molecular sieves. This type of adsorbent can eliminate 80-95% of water vapour from gas or liquid. (Azlan, 2008).

2.4.2 Silica Gel

Silica gel is a solid granular, highly porous material which is made synthetically from sodium silicate. Its chemical formula is $Si0_2.NH_2O$. It has high surface area about 550 - 800m^2/g ("Hydrates-Inhibition-Dehydration,"2009). It has been used as adsorbent due to their surfaces prefer water other than material but they cannot completely dried gas as the molecular sieves. The gel can be heated it to 120 $^{\circ}$ C once it saturated with water. During regeneration, heavy hydrocarbon can be desorbed after being adsorbed during adsorption process.

This type of adsorbents usually used in a form of bead packed in semi permeable plastic as a desiccant to control humidity to avoid degradation or spoilage some goods. It can adsorb water up to 80-95% from air, gas or liquid (Azlan, 2008).

2.4.3 Molecular Sieves

Molecular sieve is a material consists of tiny pores and uniform size that has a potential as an adsorbent for gases and liquids. Molecular sieves are crystalline metal aluminosilicates which is having a three dimensional pore system of precisely defined diameter. This structure is interconnecting network of silica tetrahedral (AlO_4) and alumina tetrahedral ($Si0_4$). The basic building blocks for zeolite structures such as Zeolites A and X are consisting of these tetrahedral (Pramatha Payra et.al, 2003).

Molecular sieves also known as syntethic zeolite which is capable to adsorb moisture more efficient compared to silica gel or clay. Highly polar surfaces within the pores distinguish its uniqueness from other adsorbents due to its ability to adsorb and remove 95-99.9% water and other polar components at very low concentrations. Molecular sieves have a uniform crystalline pores and empty adsorption cavities which are leading to the great performance in adsorption where it will not give up moisture into the package when temperature rises. Besides that, they have greater resistance to fouling and coking and they capable to remove the impurities from the process streams (Kh.Mohamadbigy, 2007). Therefore, zeolite has been chose to be used in this project since it represents many advantages compared to other adsorbents. The examples of molecular sieves are Zeolite 3A, Zeolite 4A, Zeolite 5A, Zeolite 13X and etc.

Figure 2.4: Zeolite 3A, Zeolite 4A and Zeolite 5A

2.5 ADSORBENT SELECTION

Since the molecular sieves have highly polar surfaces within the pores, it capable to adsorb and remove 95-99.9% water and other polar components at very low concentrations. This characteristic distinguishes its uniqueness from other adsorbents such as silica gel and activated alumina. Besides that, they have greater resistance to fouling and coking and they capable to remove the impurities from the process streams. For this research, Zeolite 4A and Zeolite 5A has been chosen to carry out the characterization study and dynamic performance study.

Zeolite 5A is used to remove water, hydrogen sulphide, H_2S and carbon dioxide, CO_2. Although the molecule of H_2S and CO_2 are smaller than the pore size opening of zeolite which is 5 Å (5Angstrom), the water molecules will take up into their pores first due to its high affinity towards the water. This process is called roll-up effect (Azlan, 2008). The size of water, H_2S and CO_2 are shown in figure below:

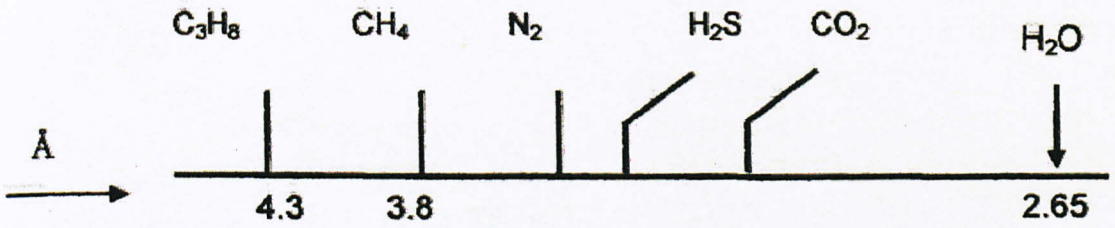

Figure 2.5: The size of the components of natural gas (Alia, 2004)

Zeolite 4A is chosen because it can adsorb and remove almost 100% water from natural gas due to its affinity (Azlan,2008) and attraction with water is strong which is it will filled up the pores with water molecules first before adsorbed other molecules that smaller than the pore opening of Zeolite 4A.

2.5.1 ZEOLITE 4A

Zeolite 4A is an alkali alumino silicate. This type of adsorbent in a sodium form which is represents the type A family of molecular sieves. The pore opening of this Zeolite is 4 Å (4Angstrom). It is usually used to adsorb water, methanol, carbon dioxide and does not adsorb any molecules larger than 4A ("What are Zeolite Molecular Sieve," 2009).

The Zeolite 4A can be obtained in pellet and sphere shapes. These are the characteristics for Zeolite 4A.

Typical properties	Unit	Value
Tapped bulk density	Kg/m^3	720
Bead size normal	mm	2-3
Crushing strength	N	40
Equilibrium water adsorption	%	22
Residual water content	%	1.5 max
Heat of adsorption	kJ/ kg water	4200
Specific heat	kJ/kg ^{o} C	1.07
Regeneration temperature	^{o} C	240 - 300

Table 2.5.1: Characteristics of Zeolite 4A

4A molecular sieve applications are used in deep drying of natural gas, air, refrigerant and alkane, static dehydration of electronic element, pharmaceutical and unstable materials, generation and purification of argon and used as desiccant for paint, dope and foul. It is also has been used for removing ethanol, carbon dioxide and ammonia which is from fluid streams. This molecular sieve is useful as a packaging desiccant for solvent dehydration. This type of this adsorbent can adsorb molecules with a diameter of less than 0.4nm (Zeochem, 2008).

2.5.2 ZEOLITE 5A

Zeolite 5A is a calcium form of A crystal type and its pore size is about 5Å (5 Angstrom) which is possess larger pore opening than Zeolite 4A. It is an alkali alumino-silicate type of adsorbents. This zeolite will adsorb molecules with a diameter less than 5 Angstrom and exclude the larger ones. It is usually used to remove water, carbon dioxide, hydrogen sulphide from sour natural gas as its strong ionic forces of divalent calcium ion makes it as an excellent adsorbent. It is also can be applied to adsorb light mercaptans ("Technical Data Sheet for Molecular Sieve," 2009).

The Zeolite 5A can be obtained in pellet and sphere shapes. These are the characteristics for both pellet and sphere Zeolite 5A.

Typical properties	Unit	Value
Tapped bulk density	Kg/m^3	730
Bead size normal	mm	2-3
Crushing strength	N	40
Equilibrium water adsorption	%	21.5
Residual water content	%	1.5 max
Heat of adsorption	kJ/ kg water	4186.8
Specific heat	kJ/kg $^{\circ}$ C	1.07
Regeneration temperature	$^{\circ}$ C	240 - 300

Table 2.5.2: Characteristics of Zeolite 5A.

Zeolite 5A is being used in producing of high purity of nitrogen, oxygen, hydrogen and inert gases from mixed gases streams. Besides, this type of zeolite usually suitable for Pressure Swing Adsorption (PSA) adsorber applications which the separation for normal and iso-paraffins (C4 to C6) purified the hydrogen and concentrated the oxygen has been applied (Zeochem, 2008).

2.6 DEW POINT

Dew point is used to express the saturation temperature of either condensable hydrocarbons or water vapour in a gas at a definite pressure. Dew point can be defined as the temperature at which the water vapour or the hydrocarbon begins to condense at constant pressure conditions (Dew Point, 2009). Figure 4 below gives the quantity of water vapour that can be present in a gas at saturation under different conditions of temperature and pressure. It is not necessarily the amount of water the gas actually does contain, but the ability of the gas to contain that amount of water given the conditions of temperature and pressure ("Glycol Dehydration and Inhibition," 2004). In the process of adsorption of water in natural gas, only the water dew point is considered.

The water content of the gas depends on the temperature and pressure of the gas. As gas pressure increases, the water content decreases and the water content will increase when temperature increases. Comparison of water content in the gas at various stages in the system will establish how much water vapour has condensed into a liquid in the pipelines ("White Paper on Liquid Hydrocarbon Drop Out in Natural Gas Infrastructure," 2005).

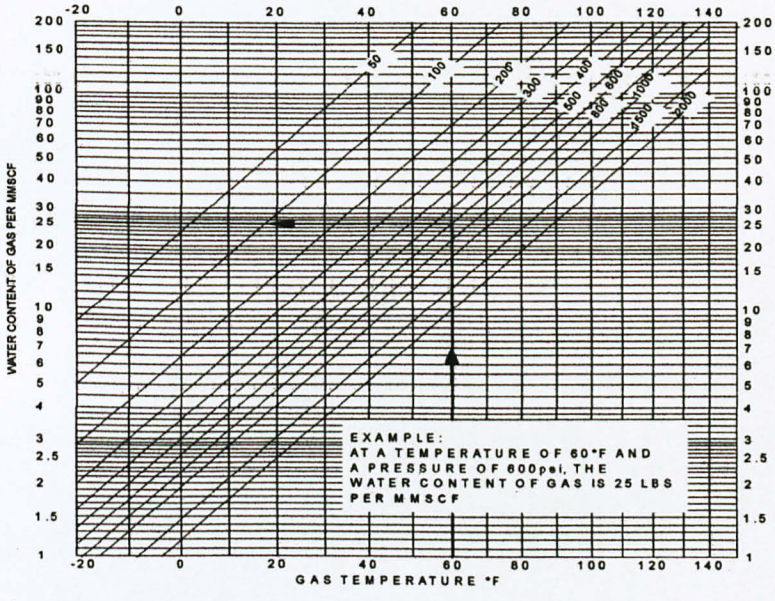

Figure 2.6.1: Water content of gas graph

Since, the function of the adsorption by zeolite is to remove water from the gas stream, the performance of the process is measured by determining the quantity of water in the outlet gas or the dew point temperature of the outlet gas.

The dew point is the temperature at which water will condense from gas. The relative water content of gas at its dew point temperature is 100%. If gas containing water vapour is cooled to a temperature so that some of the water vapour changes to liquid, the temperature at which liquid first starts to form is the dew point. When gas is at its dew point temperature, the corresponding water content at a specific pressure will be shown ("Glycol Dehydration and Inhibition," 2004).

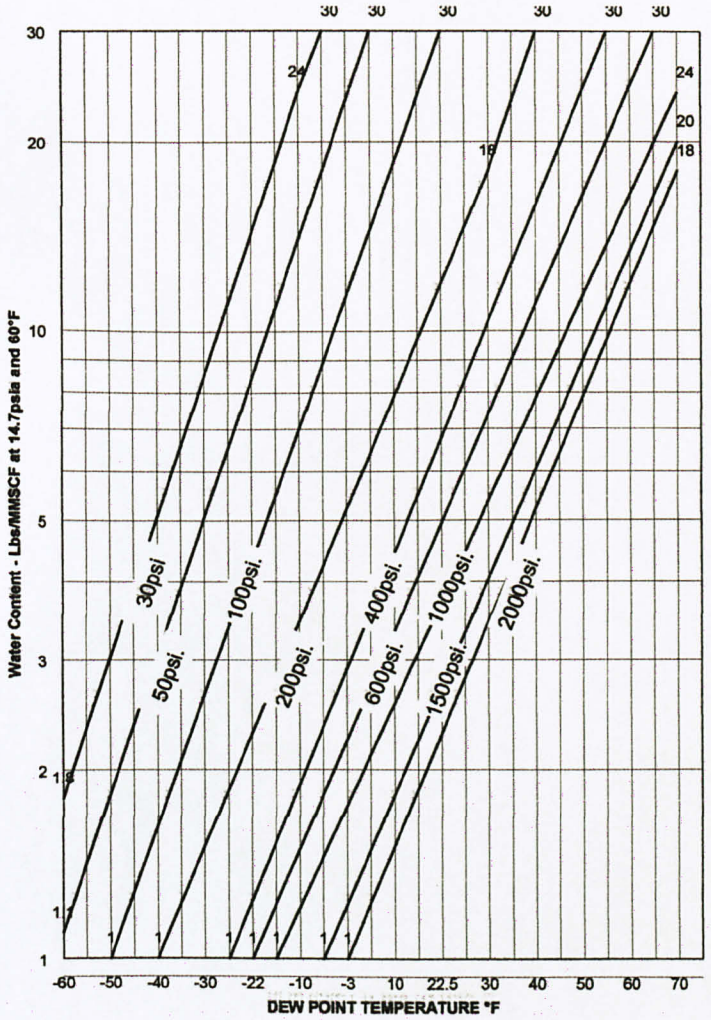

Figure 2.6.2: Dew Point graph

2.7 ADSORPTION ISOTHERMS

Adsorption isotherms are one of the important analyses for the characterization purpose. Adsorption isotherm is described as the quantity of adsorbate on the adsorbent as a function of its pressure when dealing with the gas or concentration if using the liquid at the constant temperature. The amount adsorbed is nearly normalized by the mass of adsorbent. ("Gas Phase Adsorption Isotherms," 2007)

Adsorption isotherm can be classified into six types as figure below (Kalliopi, 2006). Type I is got from an adsorbent with micropores, Type II obtained from macropores adsorbent with strong adsorbate-adsorbent interactions, Type III from macropores adsorbent with weak adsorbate-adsorbent interactions, Type IV get from macropores or mesopores adsorbent with hysteresis, Type V gained from an adsorbent with micropores or mesopores with hysteresis and Type VI is obtained in carbon blacks.

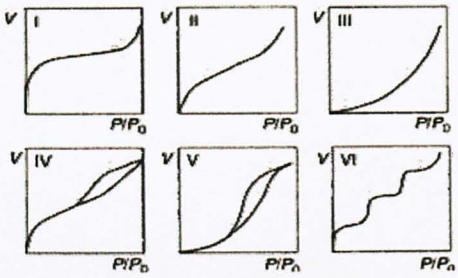

Figure 2.7: Types of adsorption isotherms

Type I isotherm is achieved when adsorption on the adsorbent's pore walls is limited to a monolayer. These isotherms are categorized when chemisorptions is occurred or when adsorbents have micropores which too small to hold adsorption in a few layers and leading to capillary condensation. Type II isotherms are referred to indefinite multi-layer formation after completion of the monolayer. Type III isotherms are referred to multilayer formation. Type IV is achieved when finite multi layer formation corresponding to complete filling of the capillaries, Type V is obtained from solids having micropores or mesopores. But Types III and IV are rare and happens when interaction between adsorbate and adsorbent are weak. While, Type VI is usually observed in carbon blacks.

2.8 THE t-PLOT

J-De Boer has made an analysis of pore structure and he discovered that the t-plot method is the great method due to a simple and direct means for interpretation purpose. T-plot analysis is based on the BET surface area and gives great information regarding the distribution of pores in the adsorbent. The t-plot or V-t curve is constructed by plotting volume adsorbed, V versus the thickness, t of the adsorbed layer (A.W.Marczewski, 2004).

The figure below shows the different types of t-plots for determining the specific surface of porous materials from the slope of the line (Kalliopi, 2006).

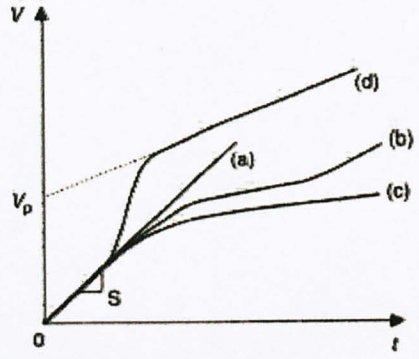

Figure 2.8: Different types of t-plot

The line a) which is a straight line represents multilayer adsorption without vapor condensation. It is indicated the thickness of the film adsorbed increases when the volume of adsorbed vapor increase where its pore surface is available for adsorption up to high pressures. The line b) indicates when micropores filled with vapor gas, the curve will drop below the straight line. It shows that there is no change in the thickness of the film adsorbed although the volume of gas increases. It is due to some of the micropores filled with the adsorbates, then part of the pore's surface unavailable for further adsorption process. In micropores where the size of the pore is comparable to the size of the gas molecule, the mechanism is different and is known as micropore filling. When the gas pressure is reduced, the gas is evaporated from the pore in reverse procedure.

The line c) shows no further adsorptions can happened when slit-shaped pores are completely filled with vapor. This line will give a smaller slope corresponding to the surface area that is still available to the adsorbent which is indicates the surface area in pores is unavailable above a certain relative pressure. The line d) tells that capillary condensation can occurred in addition to ongoing multilayer adsorption in mesopores and the curve moves away above the straight line. It shows there are only small increases in the adsorbed thickness when the amount of gas adsorbed increases.

2.9 FIXED BED ADSORPTION

A method for adsorption of the water vapour from methane gas applied fixed bed of granular particles. Gas to be treated going through the packed bed at a constant flow rate. The efficiency of adsorption depends on the system dynamics where the mass transfer resistance is important in the process of adsorption and the process is unsteady state. The concentration of water vapour and of the zeolite change with time and position (Geankoplis,2003).

Adsorption only occurs in a Mass Transfer Zone (MTZ) which moves through the bed. The Mass Transfer Zone (MTZ) width and shape depends on flowrate, adsorption isotherm, diffusion in the pores and mass transfer rate to the particles.

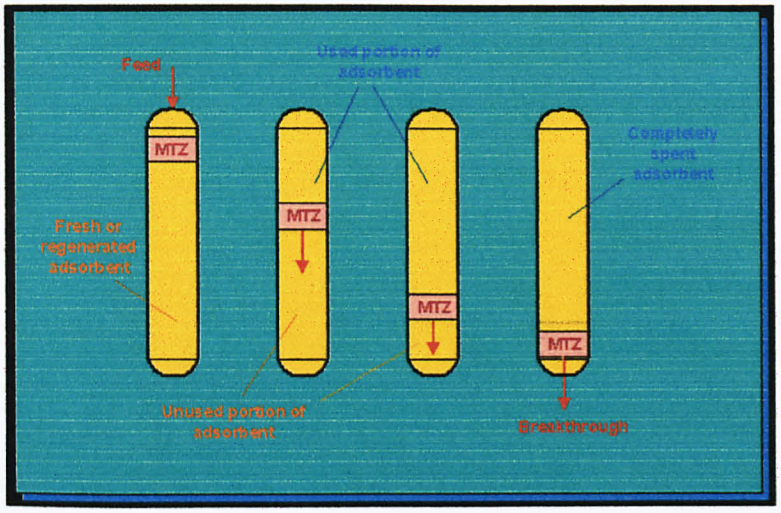

Figure 2.9.1: Mass Transfer Zone (MTZ) position in adsorption column

At the start of the process, the solid adsorbent (zeolite) is containing no solute at the inlet of the adsorption column. When the fluid comes in contact with the adsorbent, mass transfer and adsorption is take place. The concentration in fluid drops rapidly with distance as the fluid passed through the bed and it will zero before the end of column is reached.

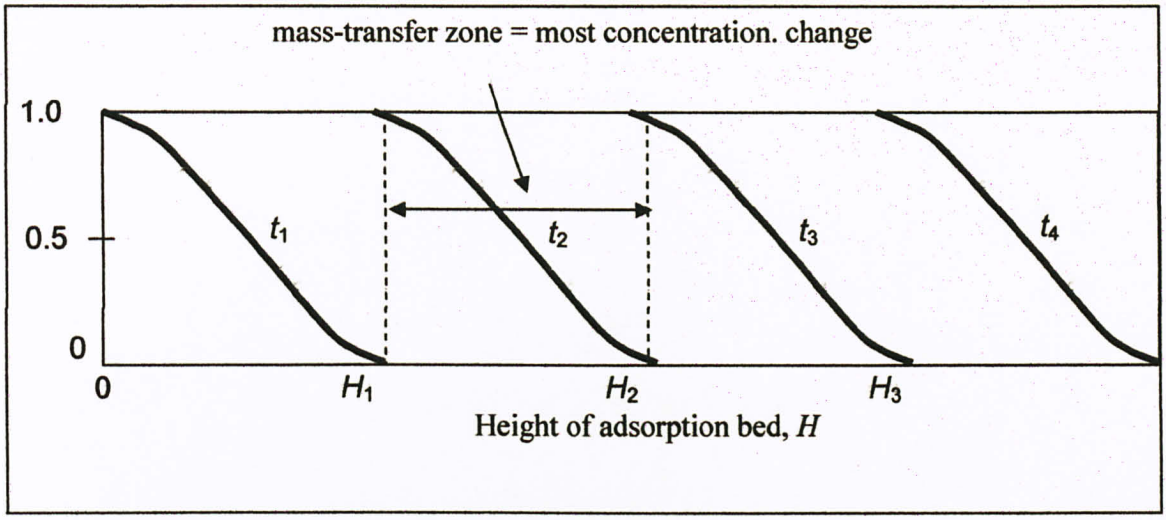

Figure 2.9.2 : Concentration profile for adsorption in a fixed bed

Stoichiometric capacity, time equivalent to stoichiometric capacity, Usable capacity up to break point time, breakthrough point, time equivalent to the usable capacity could be determined from the breakthrough adsorption curve.

The breakpoint concentration or breakthrough point, *tb* shows the maximum that can be adsorbed and usually is taken as 0.01 to 0.05 for *cb/co*. Total or stoichiometric capacity of packed-bed tower is when the entire bed reached equilibrium with the feed. This is can be calculated from area between curve and line at c/co = 1.0 (Geankoplis, 2003). Time equivalent to stoichiometric capacity is represented by the area above the curve,*tt*.

$$t_t = \int_0^{\infty} \left(1 - \frac{c}{c_0}\right) dt$$

Usable capacity, *tu* up to break point time can be determined from area between line at c/co, line at breakthrough time, *tb* and curve. Usable capacity is defined as time equivalent to the usable capacity and time at which effluent concentration reaches its maximum permissible level.

$$t_u = \int_0^{t_b} \left(1 - \frac{c}{c_0}\right) dt$$

Fraction of the total bed capacity to the break point can be represented by *tu/tt*.

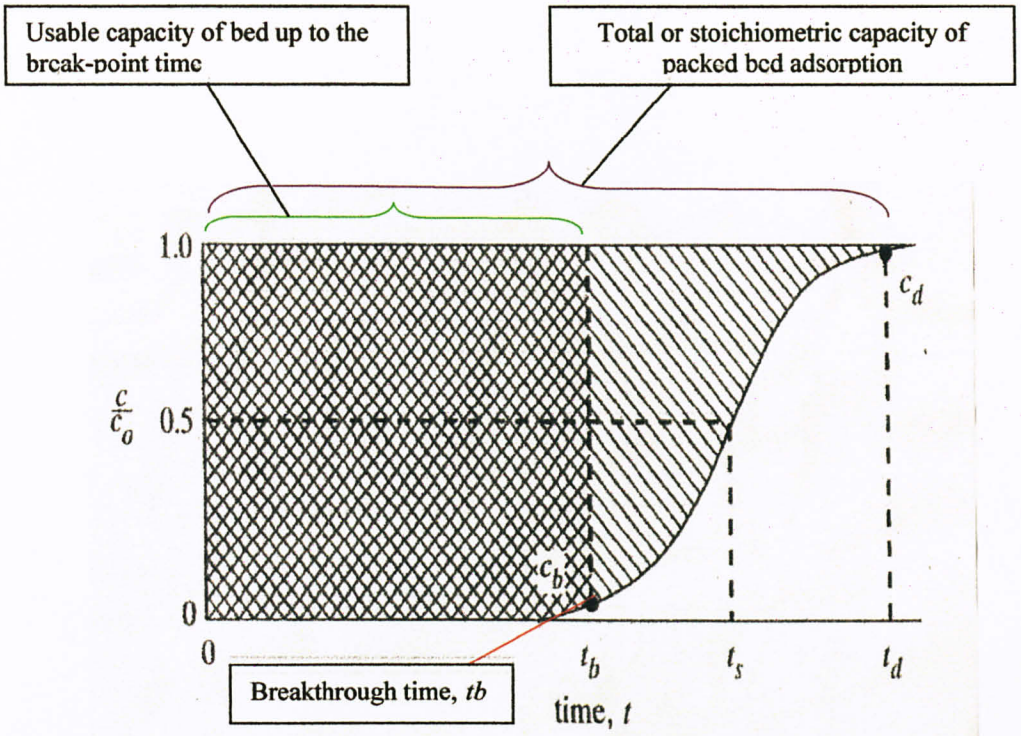

Figure 2.9.3: Determination of *tu, tt* and *tb* from breakthrough curve.

Then, used bed length (H_B), unused bed length (H_{UNB}) and total bed length can be calculated from the equation below (Geankoplis, 2003):

$$H_B = \frac{t_u}{t_t} H_T$$

$$H_{UNB} = \left(1 - \frac{t_u}{t_t}\right) H_T$$

$$\boldsymbol{HT = HUNB + HB}$$

Unused bed length (H_{UNB}) signified Mass-Transfer Zone (MTZ). It depends on fluid velocity and independent of the total length of the column.

2.10 REGENERATION OF ADSORBENT

Regeneration process is one of the important processes after adsorption process occurred. This process aims to recover adsorbate and to reuse adsorbent from adsorption process. There are several method for regeneration process such as (Geankoplis,2003):

- Pressure-swing adsorption (PSA)
- Temperature-swing adsorption (TSA)
- Inert-purge gas stripping cycle
- Displacement-purge cycle

2.10.1 Pressure-swing adsorption (PSA)

Pressure Swing Adsorption (PSA) process occurred by reducing partial pressure of adsorbate by introducing an inert gas while maintaining the total system pressure. PSA is operated close to ambient temperature because loading is increased as temperature decreased at a given partial pressure (Seader, 1998). PSA is usually applied and popular for performing bulk separation of gases which is controlled by adsorption isotherm or adsorption kinetics.

Graph below showing the effect of partial pressure on equilibrium loading at constant temperature. Reducing partial pressure from p1 to p2 causes equilibrium loading to be reduced from q1 to q2.

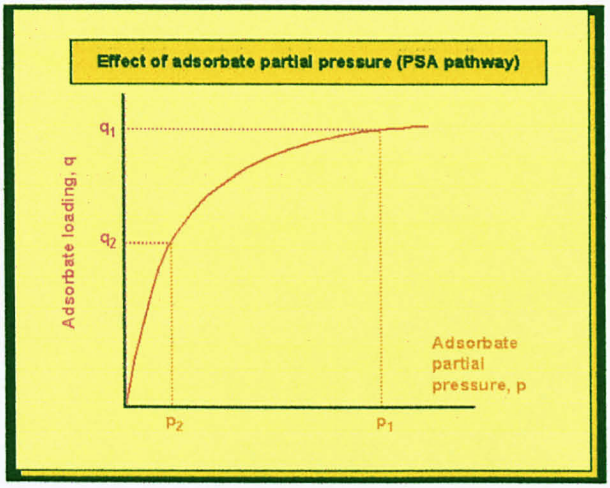

Figure 2.10.1: Pressure effect on adsorbent loading

2.10.2 Temperature-swing adsorption (TSA)

Temperature Swing Adsorption (TSA) process occurred by increasing in temperature where increasing in temperature leads to decrease in quantity adsorbed (Seader, 1998). The adsorbent is not regenerated at higher temperature than degradation temperature of material which is can cause degradation and ruin of adsorbents. TSA is operated by passaging of a hot purge gas or steam.

Graph below showing the effect temperature on the adsorption equilibrium of an adsorbate. Increasing the temperature from T1 to T2 will decrease the equilibrium loading from q1 to q2 if the partial pressure remains constant.

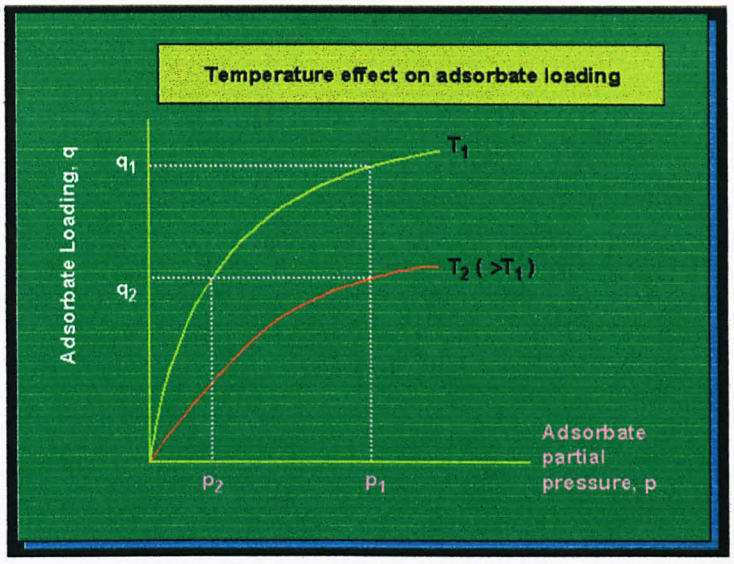

Figure 2.10.2: Temperature effect on adsorbent loading

CHAPTER 3
METHODOLOGY

There will be two research methodology involved in this project which are characterization and dynamic performance study. The objective of the characterization or screening studies is to study the physical properties such as type of structure, surface area, pore volume, pore size, composition, shape and arrangement of the pore of the selected zeolite. Dynamic performance study or parametric analysis on selected zeolite is executed aims to study the effect of the operating parameters; pressure to the performance to the process and consequently the best zolites will be determined.

3.1 CHARACTERIZATION

Investigations of the physiochemical properties of Zeolite 4A and 5A as the adsorbent for removing water from natural gas are done. A thorough searching was made through the internet and from the libraries to collect all available information regarding the properties of these zeolites and what equipments are being used for the characterization purpose. The collections of details regarding the characterization stage are essential to relate with its performance when manipulating the operating parameters and it is important factor in system design. Typically zeolite will be characterized in terms of elemental composition, structure types, surface area and thermal stability. The screening studies of zeolites will be performed as the following:

1. Physical characterization

Physical characterizations of zeolites are carried out by visual inspection. The inspection of these zeolites can be conducted by using ordinary microscope, electron microscope or raster scan electron microscope. (Clare, 2005) The shape of a crystal and the existence of crystalline impurities can be determined by the shape of materials and colour of the zeolites.

2. Structure types of zeolites

In determining the structure types of zeolites, X-ray diffraction (XRD) is used. This equipment using the x-rays with a single wavelength passed through a sample then the x-rays will be diffracted by the lattice of the crystal in order to give pattern of peak with its intensity. The x-rays will be reinforced or the beam is reinforced when its condition complied the Bragg's law (Bragg diffraction, 2009)

$$n\lambda = d \sin \Theta$$

where:

n = integer

λ = wavelength of the x-rays

d = distance between atomic layers in a crystal

Θ = angles of incidence

The samples should be crushed to the powder form before being analysed. The recorded diffraction data of samples were compared with the standard XRD pattern which is available in the library of the system (Dr Mohammad Ashraf Ali, 2004). Library system was performed in order to determine and identify the structure types of zeolites, thus it will give confirmation to the recorded data of sample one.

Figure 3.1.1: X-ray diffraction equipment

3. Pore size, pore volume and pore area distribution

Surface Area Analyzer is used to know the porosimetry by gas adsorption. In order to generate highly accurate isotherm data for material, nitrogen gas has been used and dosed precisely for both adsorption and desorption process. This instrument is ideal for the characterization of microporous and mesoporous materials.

There are two steps involved in this characterization which are degassing and analysis part. For degassing part, the sample is firstly transfer to the sample tube and attached to the degassing port before sample is being vacuumed. Vacuuming process is important to remove attached moisture in the zeolites. The analysis part required removing the mantle from sample tube and the sample tube is attached to the analysis port since the sample tube reaches the room temperature. ('Micromeritics-Analytical Instruments for Material Characterization', 2009)Then, the analysis can be run.

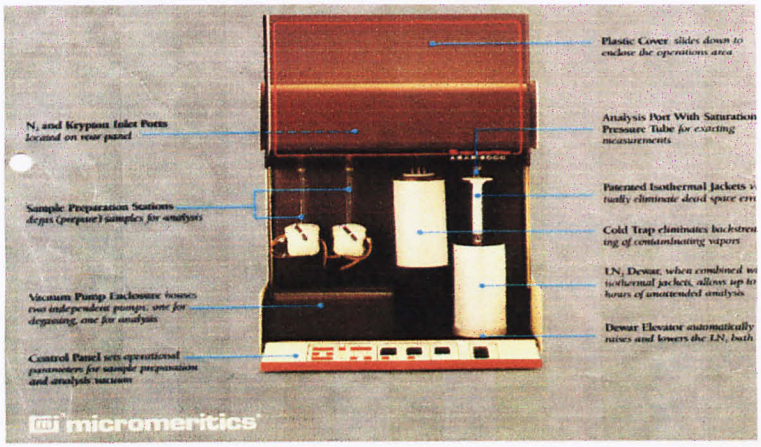

Figure 3.1.2: Surface Area Analyzer

4. Elemental analysis

Elemental analysis to determine the composition of the zeolites is carried out by using X-Ray Fluorescence (XRF). For the sample preparation, it should be crushed and grounded into a powder form by using Morta Ginder. The zeolite powder is mixed with the wax to prevent from the specimen break due to brittleness of material.

This equipment used the emission of fluorescence X-rays from a material that has been excited by attacked with gamma rays or high energy X-rays ('XRF Techniques', 2002).

Figure 3.1.3: X-Ray Fluorescence Equipment

5. Morphology (Structure, Shape and arrangement of the pore) of zeolites

Field Emission Scanning Electron Microscopy (FESEM) is executed in order to know the morphology (structure, shape and arrangement of the pore) of zeolites. FESEM technology is better than Scanning Electron Microscopes (SEM) because FESEM can visualize small arrangement of features on the surface object either entire or fractioned objects as small as 1 nanometer compared to SEM which can only visualize the objects up to 1micrometer ('FESEM',2009).

Before the sample has being analysed by the FESEM, the samples are coated by thin layer of conductive material, gold palladium to prevent detector problems in

detecting electrons. FESEM analysis will give image of structure, arrangement and shape of pore of zeolites.

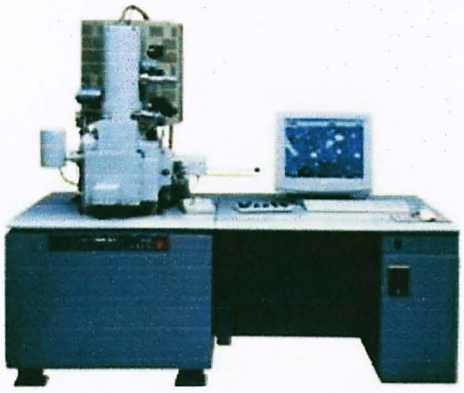

Figure 3.1.4: Field- Emission Scanning Electron Microscopy (FESEM)

6. Thermal stability of zeolites

Thermogravimetric Analyzer is being used to determine thermal stability of the zeolites (Thermogravimetric Analysis, 2009). The sample of zeolite is placed in an alumina crucible before the temperature is raised at a uniform rate of 45°C/ min up to 800 °C. This equipment performed on samples to recognize relationship weight of the zeolite with temperature (Dr Mohamad Ahraf Ali, 2004). A result of weight loss curve can be used to inform the point or spot at which weight loss is most apparent. This analysis also is carried out to determine the degradation temperature of the zeolites.

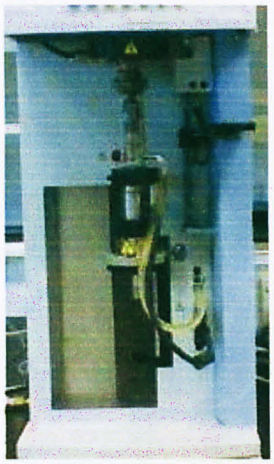

Figure 3.1.5: Thermogravimetric Analyzer

3.2 DYNAMIC PERFORMANCE STUDY

The second step for the methodology part is the analysis on dynamic performance for Zeolite 4A and Zeolite 5A. This study will be run by executing experimental work of using Gas Separation Unit while the operating parameters; pressure is manipulated during the experiment. Dynamic performance study is important to determine and study the affect of manipulating pressure to the performance of zeolites in removing water from natural gas.

Gas Separation Unit is the equipment that proficient in separating hydrocarbon and non hydrocarbon mixture such as natural gas and its impurities and volatile organic chemicals (VOC) with aiding by adsorbent such as molecular sieve and activated carbon. This unit is capable to regenerate the adsorbent by applying hot purge nitrogen gas, air or steam. Furthermore, the unit is facilitated with data acquisition and logging systems for pressure, temperature and flowrate.

This unit consists of adsorption columns, heater, saturation vessel, moisture analyzer, knockout drum vessel, data logging system, and flowmeter. (Abdurrahman, 2006). For adsorption study purpose, this unit is executed at pressure between 1 and 100bar, and desorption is performed at atmospheric and vacuum pressure.

In this experiment, the potential of Zeolite 4A and Zeolite 5A will be determined by their capability in removing water from natural gas. These findings will be measured from the water content of the water in natural gas after it goes through the zeolites. The feed composition in the experiment is methane gas. The performance of Zeolite 4A and 5A will be compared in order to determine which one has more potential and proficient in dehydrating of natural gas.

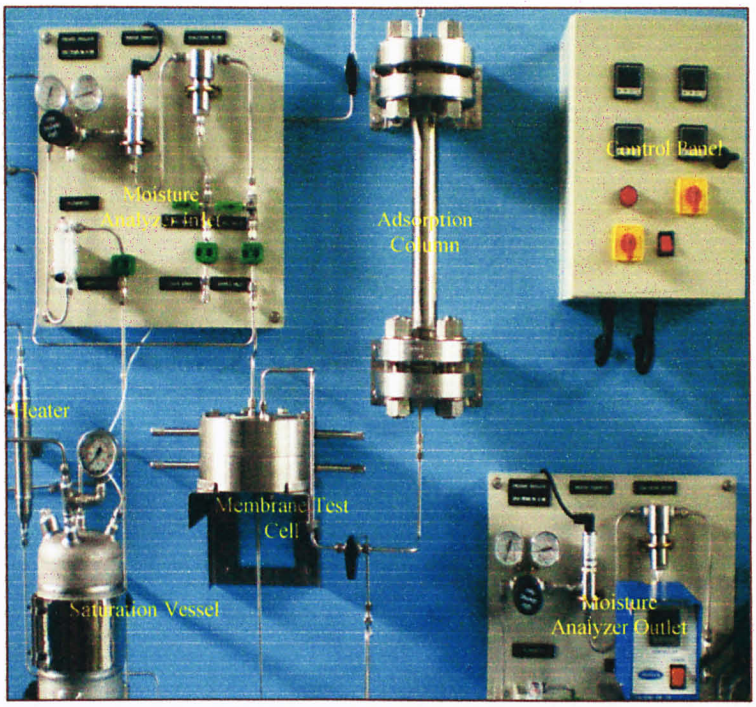

Figure 3.2: Gas Separation Unit

The details procedure for this experiment as the following:

1. Adsorbent sample is heated in a vacuum oven up to 200 °C to remove any moisture attached in the zeolites.
2. Flowrate of methane gas is set at 5LPM and 20bar for the pressure setting.
3. The methane is wetted with water vapour by passing the gas into the saturation vessel.
4. The concentration of water in the methane gas is measured by moisture analyzer which is positioned at the inlet of the adsorption column.
5. The mixture of gases flows to adsorption column.
6. Concentration of water in outlet gas is measured using moisture analyzer.
7. The adsorbed adsorbent is regenerated by using TSA where the water is ventilating out at high temperature.
8. Step 1-7 is repeated for pressure (40 and 60 bars) with constant flowrate.

These are the assumption and general ideas for the procedure above.

1. Adsorbent sample can be prepared in two ways either heating the adsorbent in vacuum oven up to 200 °C or increasing the temperature to 200 °C at the earlier experiment in order to remove moisture attached in the zeolites.
2. Gas is assumed to be saturated with water after the wetting gas phase process where the methane gas is passing into the saturation vessel that filled with water vapour.
3. Temperature Swing Adsorption (TSA) has being applied for regeneration of adsorbent where the water adsorbed by zeolites will change the phase from water to gas form. Then, the water vapour is being ventilated out.
4. Percentage of water removed from this experiment can be calculated as below:

$$\frac{\text{Water at the inlet of adsorption column - Water at the outlet of adsorption column}}{\text{Water at the inlet of adsorption column}} \times 100$$

5. Adsorption capacity of zeolites can be calculated by:

Water adsorbed = Inlet concentration of water x methane flowrate x time equivalent to total, t_t

$$\text{Adsorption capacity} = \frac{\text{Amount of water adsorbed (g)}}{\text{Weight of adsorbent (g)}}$$

CHAPTER 4
RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION

The characterization of zeolites by using Surface Area Analyzer, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Field Emission Scanning Electron microscopy (FESEM) have been performed. There are the results for those characterizations.

1. Surface area, pore size and average pore diameter

The first characterization has been done which is the experiment to determine pore size, pore volume and pore area distribution by using Surface Area Analyzer. The nitrogen gas is being used as the adsorbates for this adsorption process by Zeolite 4A and Zeolite 5A due to it has low reactivity with most solids and it is readily available as pure gas or as liquid ('Micromeritics-Analytical Instruments for Material Characterization', 2009).

The materials can be classified into three categories of its pore size (Ashleigh , 2008):

- Micropores: size of pores is less than 2nm.
- Mesopores: size of pores is between 2nm to 50nm (2nm-50nm).
- Macropores: size of pores is more than 50nm.

The first analysis is to obtain the adsorption isotherm for this experiment by plotting the graph of the volume of adsorbed gas, V versus the relative pressure for both Zeolite 4A and Zeolite 5A.

Surface area was determined from the adsorption isotherm data using BET equation ("Surface Adsorption, 2007"):

$$q/qm = KBpr / [(1-pr)(1-pr + Kbpr)]$$

where:

pr = relative pressure and

qm = represents the amount adsorbed by monolayer coverage on the surface.

From the nitrogen adsorption at liquid nitrogen temperature, the surface area of the adsorbent is determined by converting qm to the surface area. By multiplying nitrogen surface area of 3480 m2/g with qm specific surface area of the adsorbent based on nitrogen adsorption was calculated. The average pore diameter is determined using BET surface area.

$$\text{Average pore diameter} = 4V / A$$

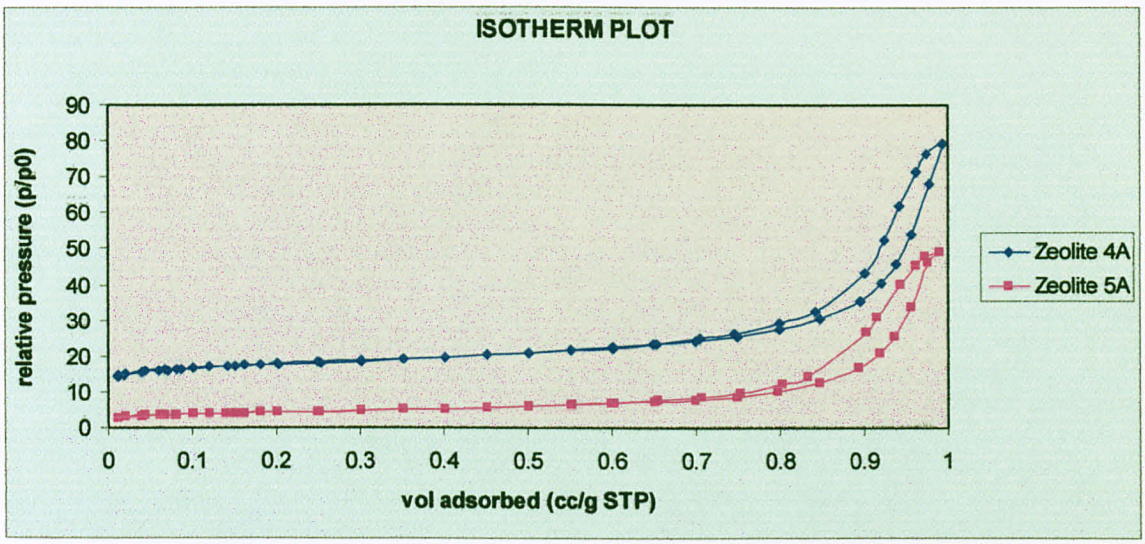

Figure 4.1.1: Isotherm plot (relative pressure versus volume adsorbed) for Zeolite 4A and Zeolite 5A.

From the isotherm plot above, we can conclude that both of zeolites are exhibit Type I isotherm which is indicates adsorption on the zeolite's pore walls is limited to a monolayer where it can hold adsorption in a few layers and leading to capillary condensation. Besides, it represents the chemisorption process is occurred for their process. Chemisorption process can be classified as an adsorption characterized by a strong interaction between an adsorbate and a substrate surface (Kalliopi, 2006).

Zeolite 4A and Zeolite 5A are represent BET surface area of 65.9890 m2/g and 14.2641 m2/g respectively. Pore diameter of Zeolite 4A is 74.1104 Angstrom and Zeolite 5A represent 10.8145 Angstrom. From these values, we can conclude that Zeolite 4A is mesopore while Zeolite 5A is micropore materials. Dr Mohammad Ashraf Ali (2004) quoted that Zeolite 5A will be give higher pore diameter and surface area but experimentally shows vice versa. It happened highly might be due to material's defect.

The second analysis is to obtain the t-plot for this experiment by plotting the graph of the volume of adsorbed gas, V versus the thickness for both Zeolite 4A and Zeolite 5A by using DeBoer equation (A.W.Marczewski, 2004)..

$$t = [13.990/(0.0340 - \log(P/P_o)]^{0.5}$$

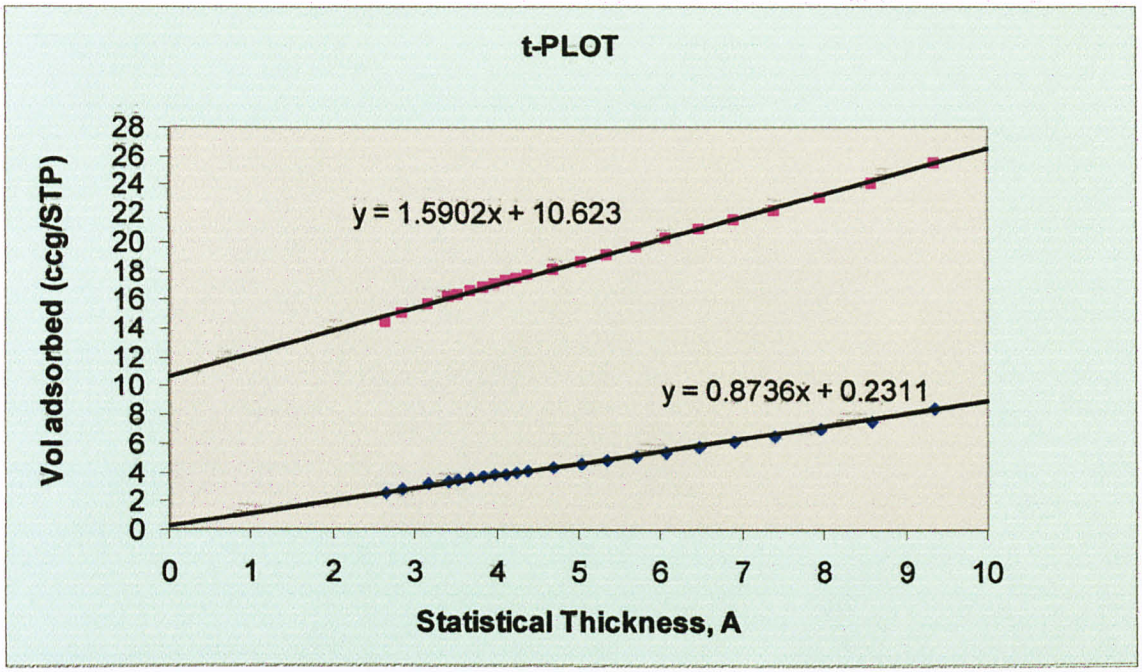

Figure 4.1.2: t- plot (volume adsorbed versus statistical thickness) for Zeolite 4A and Zeolite 5A

These t-plots will indicate the micropore volume which is can be obtained from the intercept and the slope will be giving the value of external surface area. By substituting the equation:

$$M^{WP} = Na\ V_L$$

$$S = RV_L$$

$$y = mx + c$$

$$= Rt + Na$$

$\mathbf{M^{WP}}$ = micropore volume

R = slope of the straight line

S = external surface area

Na = intercept of the straight line

$\mathbf{V_L}$ = molar volume of adsorption at the term

From the plot obtained in Figure 4.12, the micropore volume for Zeolite 4A is 0.017098 cc/g and its external surface area is 23.3940 m^2/g. While, Zeolite 5A gives the

micropore volume of 0.001115 cc/g and external surface area of 11.7871 m^2/g. Table below shows the summary of the Surface Area Analyzer's results:

Type of zeolite	Categories of pore size	BET Surface area (m^2/g)	Pore diameter (Angstrom)	Micropore volume (cc/g)	External surface area (m^2/g)
Zeolite 4A	Mesopore	65.9890	74.1104	0.017098	23.3940
Zeolite 5A	Micropore	14.2641	10.8145	0.001115	11.7871

Table 4.1: Zeolite 4A and Zeolite 5A Surface Area Analyzer's result.

2. Structure properties of zeolites

From the result obtained, unknown substance can be identified by comparing recorded diffraction data with the standard XRD pattern of molecular sieve which is available in the library system (ASTM International, 2003). The sample is being confirmed under the respective zeolite if observed peaks are similar to simulated patterns and the relative intensities of the zeolite under experiments are same as the simulated one (Dr Mohammad Ashraf et.al, 2004). Below are X-ray Diffraction pattern for both Zeolite 4A and Zeolite 5A.

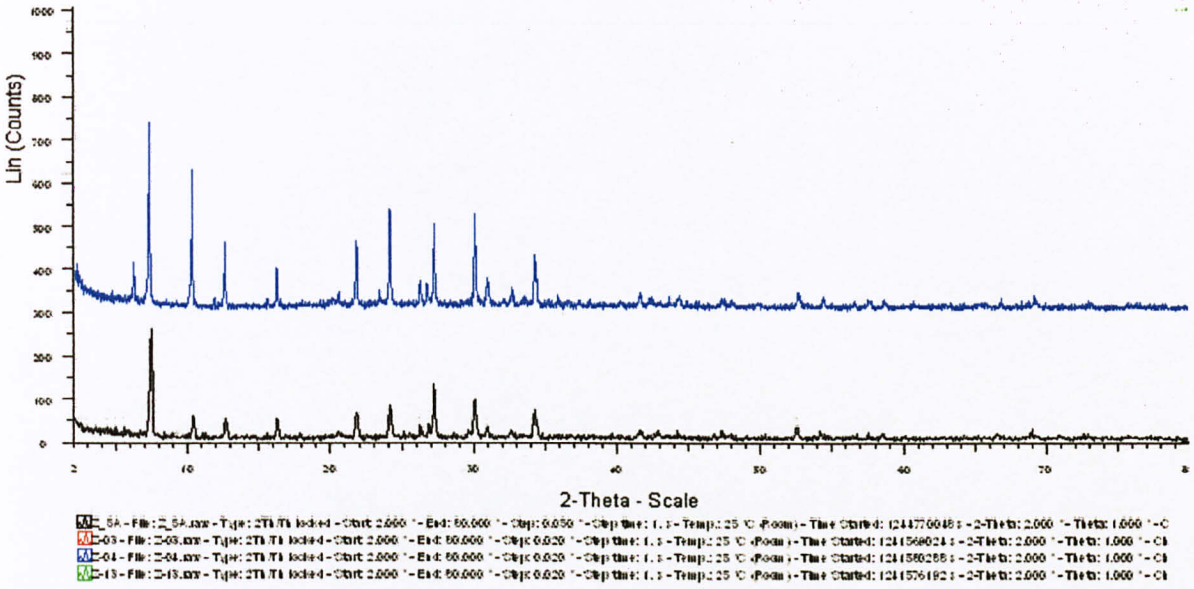

Figure 4.1.3: X-ray Diffraction pattern of Zeolite 4A (blue) and Zeolite 5A (black)

From that result, we can say that the higher intensity will give higher crystallinity. Thus, Zeolite 4A is high in crystallinity compared to Zeolite 4A because the intensities detected for Zeolite 4A is higher than Zeolite 5A. The crystal structure, lattice parameters and the interaxial angles can be determined. Zeolite 4A has the cubic crystal system with the lattice parameters of:

A= 12.27800

B = 12.27800

C = 12.27800

Since its crystal system is cubic, therefore the value of lattice parameter is equal and the value of interaxial angles is $90^{0.}$ While, Zeolite 5A also possesses the cubic crystal system with the identical lattice parameters of 24.42440 and 90^{0} of interaxial angles.

3. Elemental composition of the zeolites

The results of elemental analysis are given as below:

Composition	Zeolite 4A	Zeolite 5A
O	46.4	45.5
Na	9.5	4.12
Mg	1.31	1.43
Al	15.5	16.7
Si	23.5	20.8
P	0.111	0.0844
CI	0.00	0.104
K	0.315	0.606
Ca	2.10	9.82
Ti	0.113	0.0731
Fe	1.02	0.640
Sr	0.0108	0.0152
Cu	0.00	0.0180
Cr	0.00	0.00
Ni	0.00	0.00
Zn	0.00	0.00

Table 4.2: Elemental analysis for Zeolite 4A and 5A

Notes: Yellow cell indicates highest composition

From the table above, Zeolite 4A is mainly consist of Oxygen, Silicon, Aluminium and Sodium with highest percentage Sodium. While, Zeolite 5A is primarily consists of Oxygen, Silicon, Aluminium and Calcium with highest percentage of Calcium. Since the basic building blocks structure of zeolite is interconnecting network of alumina tetrahedral (AlO_4) and silica tetrahedral ($Si0_4$) (Pramatha, 2003), therefore it is confirmed by the elemental analysis that Zeolite 4A is a sodium form while Zeolite 5A is a calcium form.

4. Morphology (Structure, Shape and arrangement of the pore) of zeolites

The morphology of both zeolites has been investigated in order to observe and identify their changes and differences. This characterization has been done with magnification of 100 K with range of scale is 100 nanometre(10^{-9}) since the pore size of zeolites in unit of Angstrom (10^{-10}). These are the image for the Zeolite 4A and 5A:

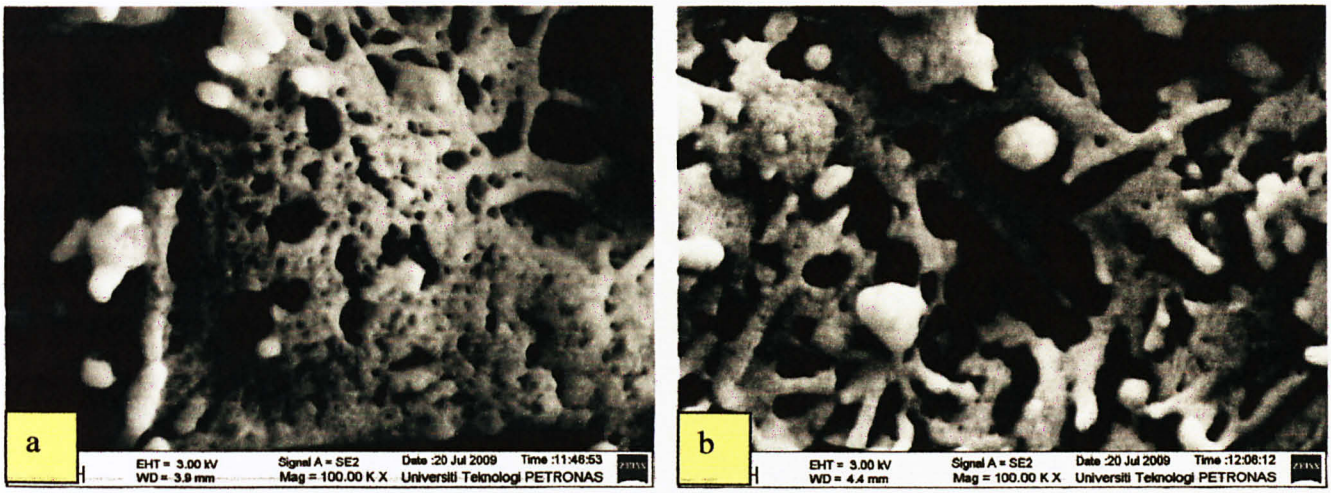

Figure 4.1.4: FESEM image of a) Zeolite 4A and b)Zeolite 5A

From figure above, pores and interconnecting pores of Zeolite 5A is seems bigger than Zeolite 4A. Interconnecting pores is representing the permeability which is the easiness flow of the fluid in the zeolites.

5. Thermal stability of zeolites

The thermal stability of Zeolite 4A and Zeolite 5A has been assessed in order to determine the degradation temperature, regeneration temperature which is the point where the water can be removed from the pore of zeolite and percentage of weight loss when the temperature increases during the experiment.

Thermograms obtained for the both zeolites as below:

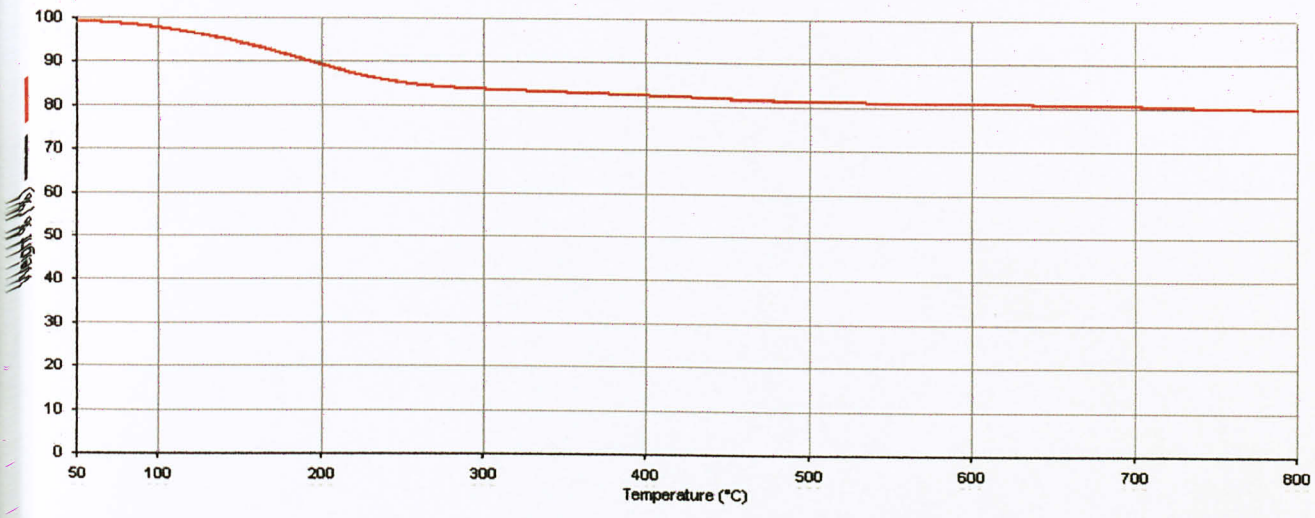

Figure 4.1.5 : Thermograms of Zeolite 4A

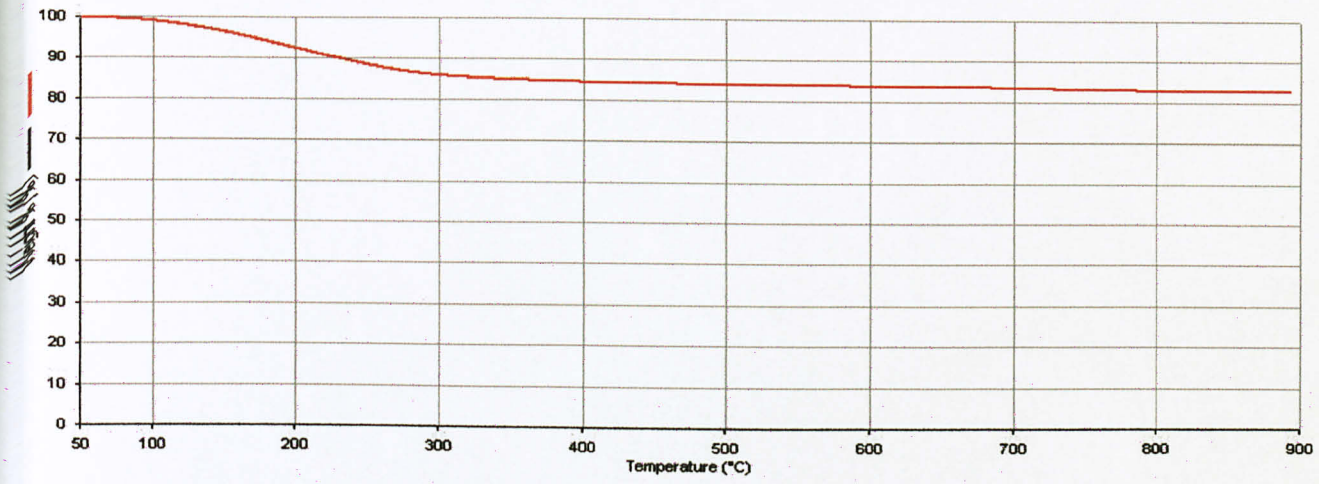

Figure 4.1.6: Thermograms of Zeolite 5A

From figure above, Zeolite 4A and Zeolite 5A were found can take up the moisture up to 300-400 ° C. But, Zeolite 4A can remove moisture at higher temperature than Zeolite 5A because from the Figure 4.1.7 and Figure 4.1.8, we can see Zeolite 4A is still able to remove moisture up to 500 ° C. Both molecular sieves not undergo any mass loss except the decomposition of moisture nor degradation of material occurred up to 900 ° C (Prabir K.Patra et.al, 2002). The weight loss of both molecular sieves is due to moisture decomposition. The calculation of weight loss is as below:

$$\text{Percentage of weight loss} = \frac{\text{Initial weight of zeolite} - \text{Last weight of zeolite}}{\text{Initial weight of zeolite}} \times 100$$

The percentage of weight loss for zeolites and copper catalyst is summarized as table below:

Sample	Thermal stability (° C)	Wt% loss in the range 45 - 900 ° C
Zeolite 4A	> 900	23.054
Zeolite 5A	> 900	17.219

Table 4.3: Percentage of Weight Loss of the Samples

4.2 DYNAMIC PERFORMANCE STUDY

The purpose of performing Dynamic Performance Study is to study the effect of the pressure variation towards to the performance of the system. The experiment will be operated at constant temperature and flowrate and the pressure will be manipulated from range of 20-60 bars for all selected adsorbents. The experiments will be executed by using Gas Separation unit system.

4.2.1 Calibration

Prior carrying out the experiment, the calibration is performed in order to determine the best flowrate and temperature to be used while varying the pressure. The accuracy of the flow meter equipped in this system is about 1% full scale. An error of 10% is introduced in the flowmeter reading if performing the flowate at`1L/min. Normally, the acceptance error by the measurement is only 5% (Montgomery, 2005). It would be difficult to analyze the result if the flowrate exceeds 7L/min due to the breakthrough time would be very fast. Flowrate at 4-6 L/min was found that the measurement and reading can be performed with good accuracy and analysis of the result can be analyzed (Abdurrahman, 2006). Thus, the flowrate of 5L/min was determined as the most suitable flow rate while error of measurement is still reasonable. The percentage of valve opening is set for the adjustment of the flowrate.

Calibration experiment was carried out at different temperature and pressure in order to find the best temperature that giving the most moisture content. Temperature at ranges 45 – 55 ° C was found that the measurement and reading can be performed with good accuracy. Below is the result for calibration experiment:

Flowrate of methane gas (L/min)	Temperature (° C)	Pressure (barg)	Concentration of water (ppmv)
5	40	20	923.389
		40	410.756
		60	270.755
	45	20	923.389
		40	429.655
		60	285.064
	50	20	1100.570
		40	469.756
		60	317.696

Table 4.2.1: Moisture content at different temperature and pressure; constant flowrate

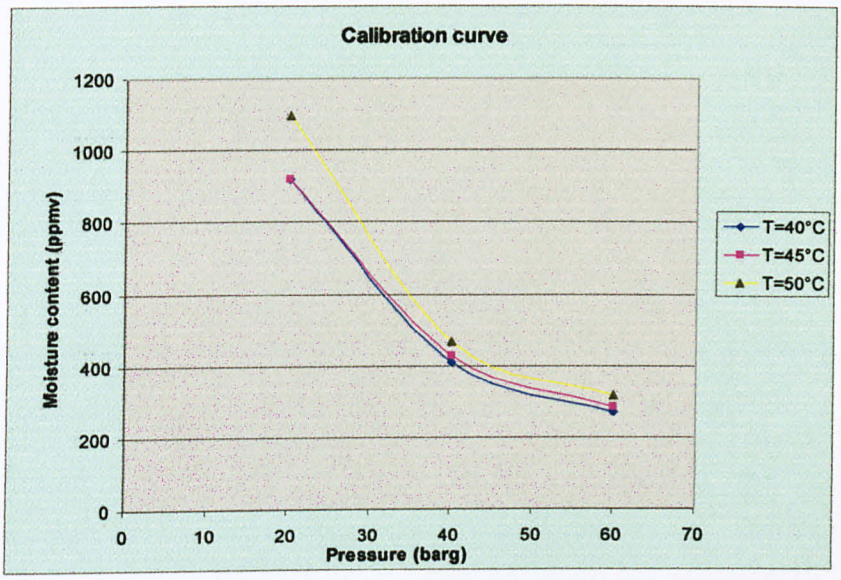

Figure 4.2.1: Calibration curve

From calibration curve above, it was found that the pressure is inversely proportional to the concentration of water where as the pressure increases, concentration of water decrease. The water content increases with increases of temperature which is represent that the temperature is directly proportional to the content of moisture. Thus, the temperature of 55 ° C is selected as a temperature setting to run experiment because it indicates highest moisture content.

4.2.2 Dynamic Adsorption Study

The main reason of the dynamic study is to study the affect of pressure to the performance of the system and chosen the best zeolite regarding the ability of removing water from natural gas. The performance of the system is evaluated based on adsorption capacity and percent of water removal by zeolites. Detail calculation regarding adsorption capacity and percent removal of water is given in Appendix B. In this experiment, the pressure is manipulated for 20, 40 and 60 bars while other parameters such as temperature and flowrate remained constant at 50°C and 5 NLPM respectively. The concentration profile for both zeolite at each pressure is plotted in order to determine the breakthrough time, t_b and time to total stoichiometry, t_t. The breakthrough concentration profiles for both zeolites are given in the Figures 4.2.2 to 4.2.7 below:

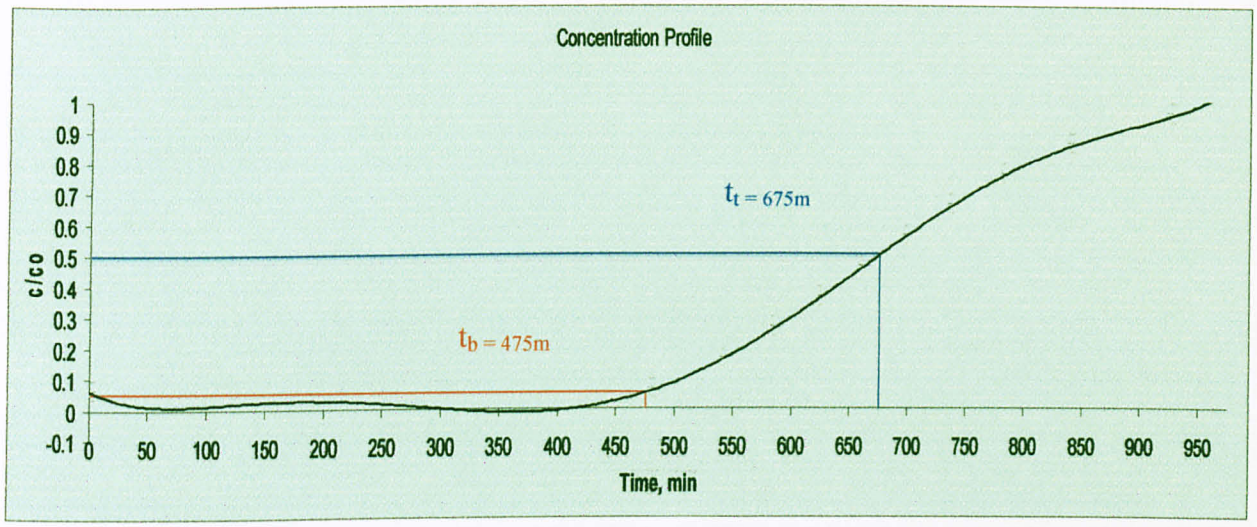

Figure 4.2.2: Concentration profile for Zeolite 4A at pressure=20bar

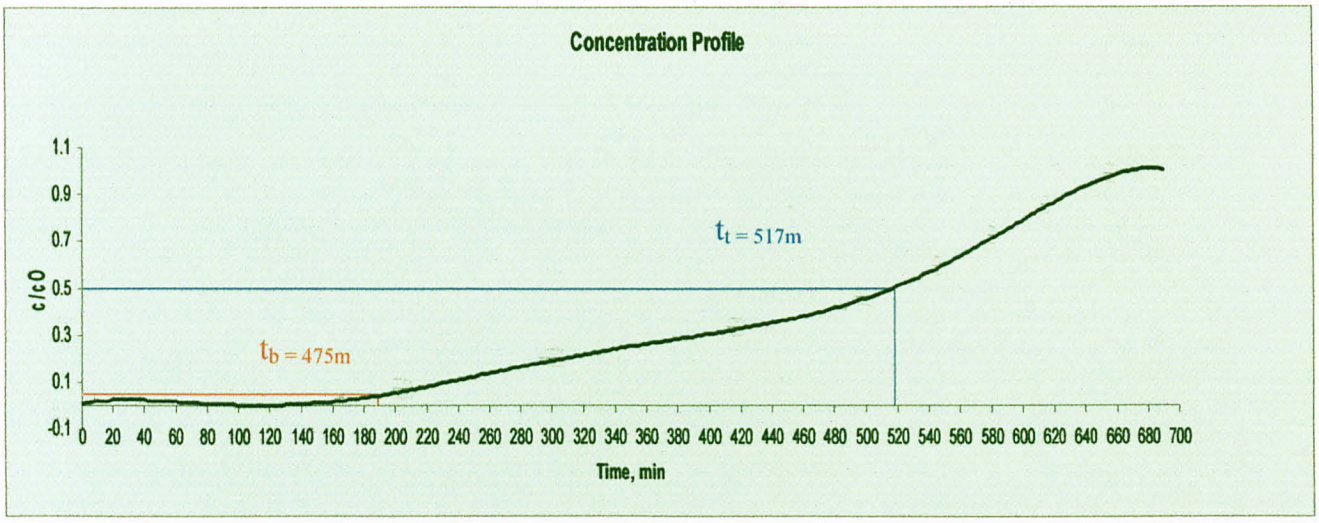

Figure 4.2.3: Concentration profile for Zeolite 4A at pressure=40bar

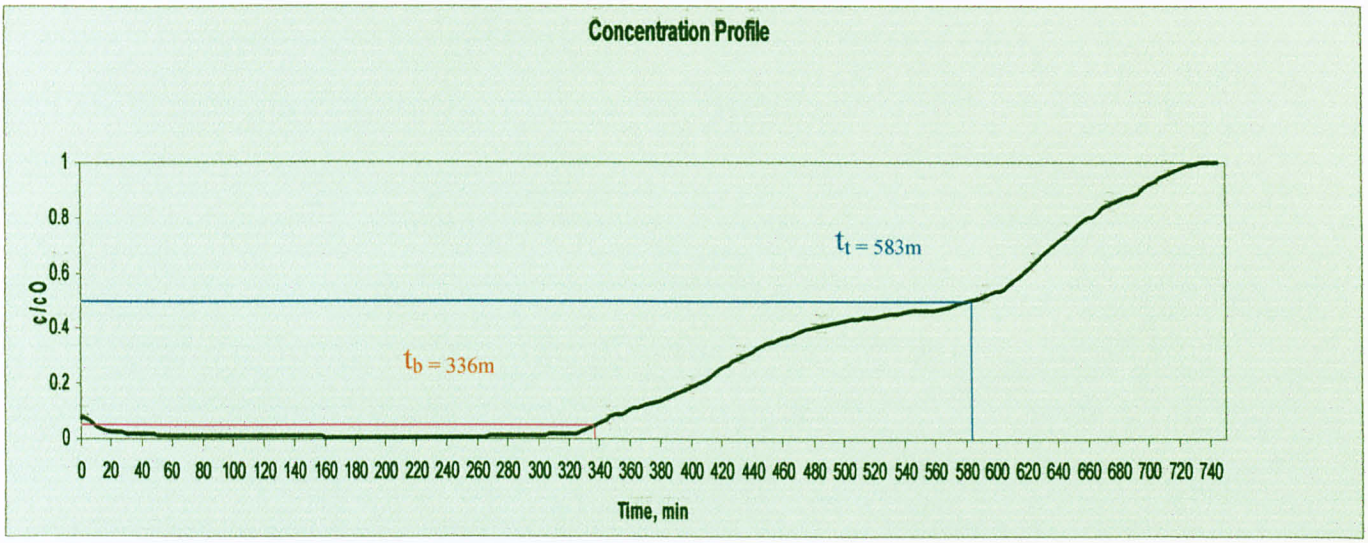

Figure 4.2.4: Concentration profile for Zeolite 4A at pressure=60bar

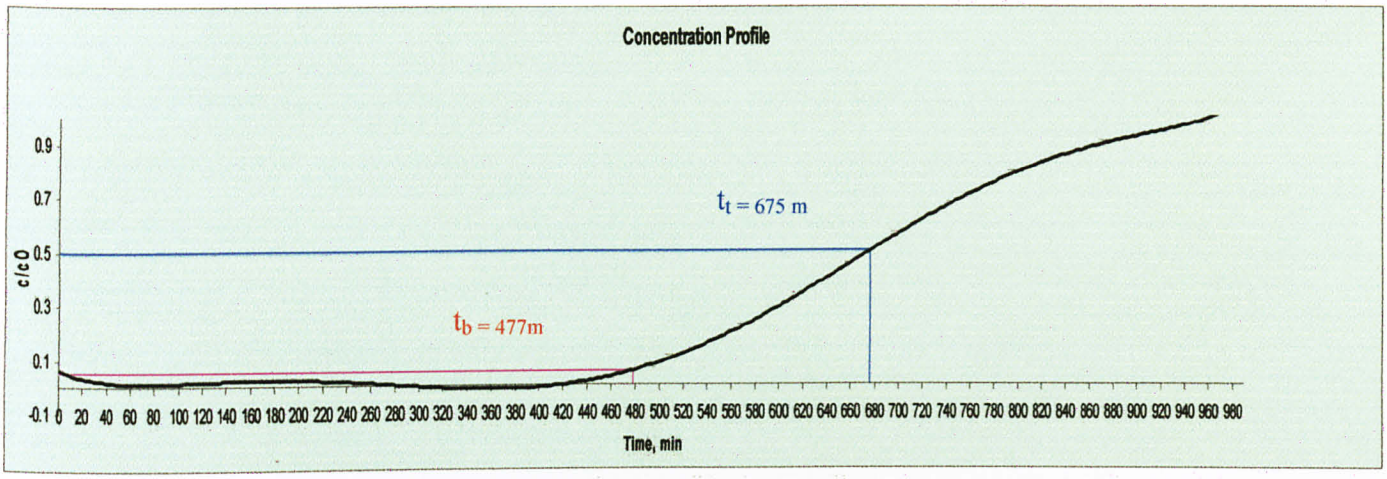

Figure 4.2.5: Concentration profile for Zeolite 5A at pressure=20bar

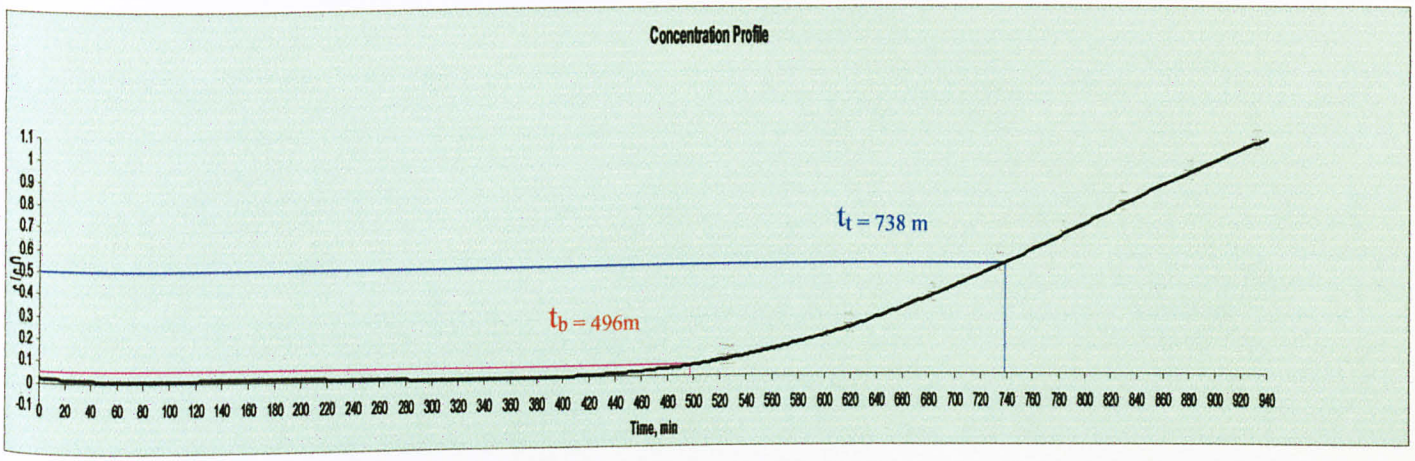

Figure 4.2.6: Concentration profile for Zeolite 5A at pressure=40bar

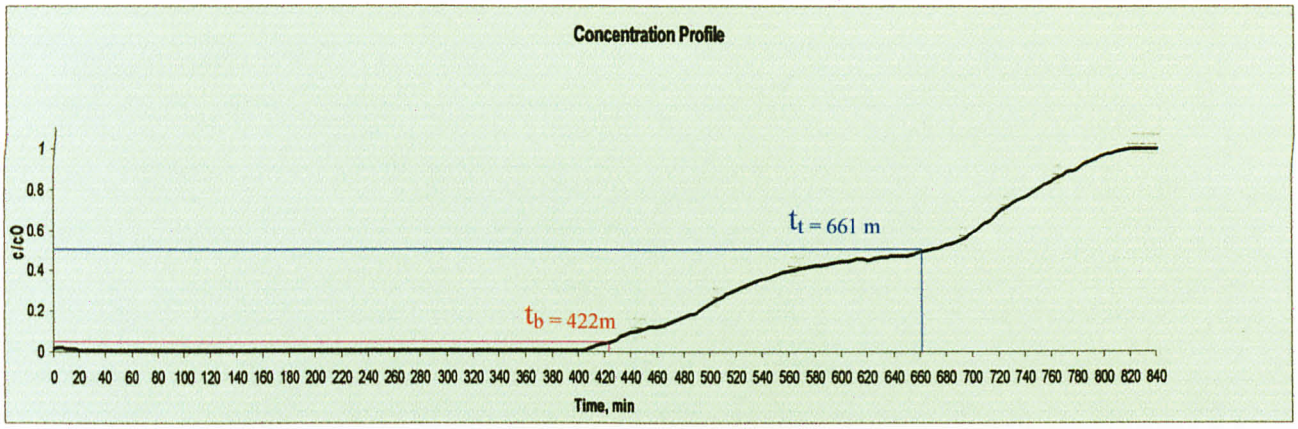

Figure 4.2.7: Concentration profile for Zeolite 5A at pressure=60bar

The value of breakthrough time, t_b indicates time equivalent to the usable capacity which is at the point the effluent concentration reaches its maximum permissible level. The time equivalent to total or stoichiometric capacity represent by t_t . t_t value indicates when the entire bed comes equilibrium with the feed which is can be represented by the area above the curve. The result for the experiment can be summarized as the table below:

Criteria / Adsorbent	Zeolite 4A			Zeolite 5A		
	20	40	60	20	40	60
Breakthrough time, t_b (min)	475	187.4	336	477	496	422
Time equivalent to total, t_t (min)	675	517	583	675	738	661
Time to achieve c/c_o=1, t_d (min)	975	690	745	970	940	840
Used bed, H_B (cm)	21.11	10.87	17.29	21.2	20.16	19.15
Unused bed length, H_{UNB} (cm)	8.89	19.13	12.71	8.8	9.84	10.85
Total water adsorbed (g)	2.0576	1.019	0.7721	2.0576	1.4541	0.8755

Adsorbent capacity (g/g)	0.005415	0.002681	0.002032	0.005415	0.003827	0.002304
Percentage removal of water (%)	98.97	99.34	98.89	99.35	99.57	95.91

Table 4.2.2: Summary of result for both zeolite at different pressure

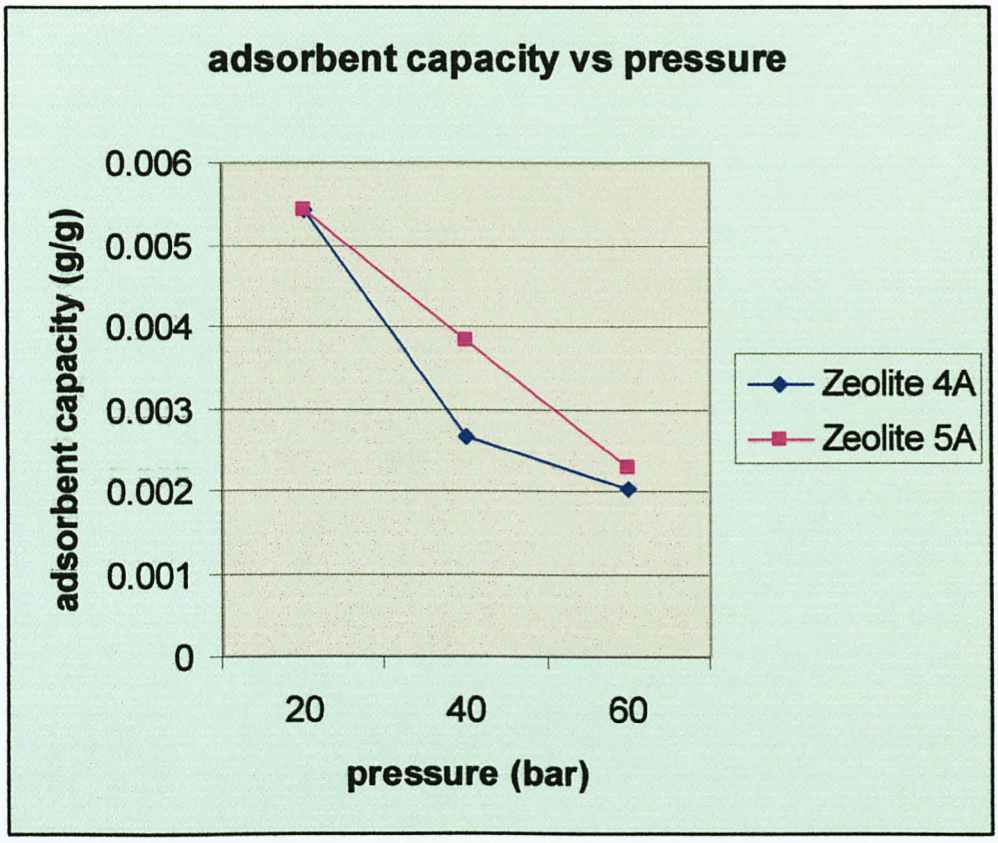

Figure 4.2.8: Plot of adsorbent capacity at different pessure

It is obtained from the concentration profile that the concentration of solute in the fluid phase and of the solid adsorbent phase change with time as gas passed down through the bed at constant flowrate. The concentration water in methane gas drops with distance and zero before end and then the concentration will be increased after it has achieve breakthrough time. As the pressure increases, the breakthrough time, t_b time equivalent to total stoichiometric capacity, t_t and the time taken to achieve $c/c_0=1$ is decreased.

From the graph above, we can concluded that it is preferable to perform adsorption at low pressure since at low pressure, more water can be absorbed from methane gas. This is can be determined from the total water adsorbed and adsorbent capacity where it is favourable to execute adsorption at low pressure. High pressure will give high diffusivity of water on zeolite surface where the adsrobate will move faster through the packed bed. The residence tme for the solute interacts with the adsorbent is reduced and it is not long enough to achieve equilibrium. Therefore, the adsorbate will leaves the adsoption column before equilibrium occurs.

The adsorbent that give better result in removing water is Zeolite 5A since it gives higher total water adsorbed and adsorption capacity compared to Zeolite 4A. This is due to the high affinity towards water of Zeolite 5A compared to Zeolite 4A. Even though the result from Surface Area Analyzer shows Zeolite 4A has higher surface area which is indicates larger space for the adsorbate to attach, but since the affinity towards water of Zeolite 5A is higher, thus it can adsorb more water from methane compared to Zeolite 4A.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

It is essential to find other alternatives to remove water from natural gas to overcome the problems when deals with TEG system. TEG system needs bigger space and equipment for installment, where there is limited space in offshore platforms. Dehydration of natural gas by using zeolite is one of the alternatives to remove water from natural gas at offshore platforms. Preliminary study and literature review has proved that Zeolite 4A and Zeolite 5A have a potential to become a good adsorbent in removing water from natural gas.

From Surface Area Analyzer result, Zeolite 4A and Zeolite 5A can be categorized as mesopore and micropore materials since their pores range is between 2nm to 50nm and less than 2nm respectively. Zeolite 4A has higher surface area, pore diameter, micropore volume and external surface area compared to Zeolite 5A. Both of zeolites exhibit monolayer adsorption. XRD shows that both of Zeolites are in crystalline phase but Zeolite 4A is high in crystallinity compared to Zeolite 5A. Both of the zeolites are cubic crystal system with identical lattice parameters and interaxial angles.

Zeolite 4A has been confirmed is a sodium form while Zeolite 5A is a calcium form from XRF result. FESEM image shows that pore size and interconnecting pores of Zeolite 5A seems bigger than Zeolite 4A has. This image proved that existence of cation could cause some changes in the structure and properties of zeolites. TGA analysis of molecular sieves not undergoes any mass loss except the decomposition of moisture nor degradation of material occurred up to 900 $^{\circ}$ C. Zeolite 4A can remove moisture at higher temperature than Zeolite 5A.

Dynamic Performance study give a result that it is favorable to operate the adsorption process by zeolite since it give higher adsorption capacity and total water of

removal from natural gas. Zeolite 5A is found give better performance in removing water from natural gas than Zeolite 4A due to its affinities towards water.

As the conclusion, the objective to analyze the performance of zeolites under various operating pressure is achieved.

5.2 RECOMMENDATIONS

There are some recommendations that can be made for this study. Based on the results that we obtained from the experiment, it is recommended that the optimum pressure can be determined by optimization based on cost analysis to maximize water vapour removal and minimize hydrocarbon loss for the next study.

Beside that, in order to reduce condensation, t is recommended to install a heater right before adsorption column inlet and moisture analyzer. For thermal stability measurement of zeolites , it is recommended to use Thermogravimetric Analyzer (TGA) that can measure the temperature more than 900 °C so that the degradation temperature of zeolite can be determined precisely.

In this project, moisture analyzer has been used in determining the water content after passing through the saturation vessel (inlet) and at the outlet of the gas. But for getting better result of exact amount of water in the methane, it is better to use Karl Fischer titration. This titration method uses coulometric or volumetric titration in determining trace amounts of water in a sample.

Besides that, the zeolite should be kept securely to prevent it from adsorb moisture from atmosphere like keeping the zeolites in the container containing silica gel.

Figure 5.2 : Karl Fischer titration

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APPENDIX A:

SURFACE AREA ANALYZER RESULT

A 1: Experimental data for characterization section: Isotherm plot (volume adsorbed versus relative pressure) for zeolite 4A.

Volume adsorbed	relative pressure
14.3664	0.0101
14.9846	0.0197
15.6821	0.0423
16.1276	0.0666
16.3341	0.08
16.6019	0.1001
16.8346	0.1203
17.0624	0.1405
17.2689	0.1605
17.4738	0.1804
17.6687	0.2003
18.128	0.2489
18.6314	0.3006
19.1451	0.3508
19.6624	0.3996
20.2193	0.4494
20.8281	0.4994
21.475	0.5495
22.1838	0.5992
23.0318	0.649
24.0917	0.6988
25.4692	0.7486
27.3808	0.7981
30.3187	0.8469
35.427	0.8946
40.0268	0.9198
45.4745	0.9379
53.9609	0.9562
68.0219	0.976
79.0417	0.9937
76.1172	0.9728
71.3518	0.9614
61.6827	0.9415
52.139	0.9227
43.1364	0.8992
32.4271	0.8404
28.8346	0.7982
26.0693	0.7442

Molecular sieve: Zeolite 4A

Weight: 0.3711 gram

Free space: 51.1994 cc

23.3809	0.6517
22.3801	0.6008
21.5645	0.5503
20.8591	0.5003
20.1325	0.4505
19.4898	0.4007
18.9243	0.3498
18.3965	0.3002
17.8985	0.251
17.3496	0.2012
16.8851	0.1507
16.1194	0.0865
15.8661	0.069
15.7088	0.0598
15.2915	0.04
14.5551	0.0182
13.9448	0.0101

A 2: Experimental data for characterization section: t- plot (volume adsorbed versus statistical thickness) for zeolite 4A.

Volume adsorbed	statistical thickness
14.3664	2.626
14.9846	2.836
15.6821	3.153
16.1276	3.4
16.3341	3.517
16.6019	3.679
16.8346	3.83
17.0624	3.973
17.2689	4.109
17.4738	4.241
17.6687	4.371
18.128	4.683
18.6314	5.016
19.1451	5.349
19.6624	5.688
20.2193	6.057
20.8281	6.457
21.475	6.898
22.1838	7.386
23.0318	7.942
24.0917	8.589
25.4692	9.358
27.3808	10.297

Molecular sieve: Zeolite 4A

Weight: 0.3711 gram

Free space: 51.1994 cc

A 3: Experimental data for characterization section: Isotherm plot (volume adsorbed versus relative pressure) for zeolite 5A

Molecular sieve: Zeolite 5A

Weight: 0.7406 gram

Free space: 53.2406 cc

Volume adsorbed	relative pressure
2.4932	0.0103
2.7921	0.0199
3.1213	0.0426
3.3301	0.0668
3.4198	0.0794
3.5466	0.0997
3.6594	0.1199
3.7631	0.1399
3.8626	0.1599
3.9577	0.1799
4.0504	0.2
4.2717	0.2489
4.5243	0.3005
4.7924	0.3507
5.0753	0.3996
5.386	0.4495
5.7178	0.4995
6.0657	0.5494
6.4696	0.5989
6.95	0.6492
7.5563	0.6986
8.4414	0.7479
9.8715	0.7969
12.26	0.8462
16.4768	0.8925
20.7982	0.9187
33.6507	0.9561
45.9548	0.9745
48.7872	0.9893
47.4933	0.9708
45.1785	0.9601
39.7901	0.9431
30.561	0.9148
26.5224	0.9021
14.116	0.8326
11.8287	0.8025
9.5424	0.7526
8.2254	0.7047
7.3482	0.6534
6.7563	0.6021
6.301	0.5513
5.9032	0.5005
5.5223	0.4503
5.1726	0.3998
4.8639	0.3498
4.5811	0.3001
4.3188	0.2499
4.0744	0.1999
3.8293	0.15
3.5538	0.1002
3.4245	0.0798
3.2777	0.0599
3.0846	0.04
2.7865	0.0204
2.4831	0.0103
5.1726	0.3998

A4: Experimental data for characterization section: t- plot (volume adsorbed versus statistical thickness) for Zeolite 5A.

Volume adsorbed	thickness
2.4932	2.631
2.7921	2.839
3.1213	3.156
3.3301	3.401
3.4198	3.512
3.5466	3.676
3.6594	3.827
3.7631	3.969
3.8626	4.105
3.9577	4.238
4.0504	4.369
4.2717	4.683
4.5243	5.015
4.7924	5.349
5.0753	5.688
5.386	6.058
5.7178	6.458
6.0657	6.897
6.4696	7.384
6.95	7.945
7.5563	8.587
8.4414	9.346
9.8715	10.272

Molecular sieve: Zeolite 5A

Weight: 0.7406 gram

Free space: 53.2406 cc

APPENDIX B:

DYNAMIC PERFORMANCE STUDY

B1: Calculation for breakthrough time, time equivalent to total stoichiometric capacity, used bed, unused bed, total bed, adsorption capacity and percentage removal of water methane gas.

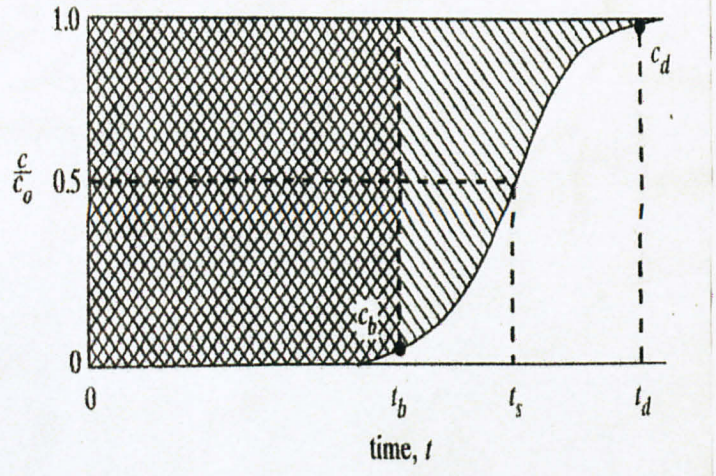
Example : Zeolite 4A at pressure 20 bar.

Breakthrough time or time equivalent to usable capacity :

$$t_u = \int_0^{t_b=3.65} (1-\frac{c}{c_0})dt \quad = A_1 = t_b = 475 \text{ min}$$

Time equivalent to total stoichiometric capacity:

Assume breakthrough curve is symmetrical at *c/co* at *ts*. *ts* = *tt*. Therefore, area below curve between *tb* & *ts* = area above curve between *ts* & *td*



Therefore,

$$t_t = \int_0^{\infty} (1-\frac{c}{c_0})dt \quad = A_1 + A_2 = t_e = 675 \text{ min}$$

Length of Used bed:

$$H_B = \frac{t_u}{t_t} H_T \quad = (475 / 675) \text{ x } 30\text{cm} = 21.11 \text{ cm}$$

Length of Unused bed:

$$H_{UNB} = (1 - \frac{t_u}{t_t}) H_T \quad = (1 - (475 / 675)) \text{x } 30\text{cm} = 8.89 \text{ cm}$$

Total Length of bed:

$H_T = H_{UNB} + H_B = 30$ cm

Adsorption capacity of zeolite :

- Methane flow rate = 203.999 g/h
- Inlet water concentration = 896.5424 ppm
- Time equivalent to total stoichiometric capacity = 675 min = 11.25 h

Total water adsorbed = (896.5424 / 1000000) x 203.999 g/h x 11.25 h

= 2.057564 g

Mass of adsorbent = 380 g

Adsorption capacity = (2.057564 / 380)

= 0.005415

APPENDIX C:

P&ID OF GAS SEPARATION UNIT